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HEATS OF REACTIONS OF SOME OXIDES OF AMERICIUM AND PRASEODYMIUM WITH NITRIC ACID AND AN ESTIMATE OF THE POTENTIALS OF THE Am(III)-Am(IV) AND Pr(III)-Pr(IV) COUPLES
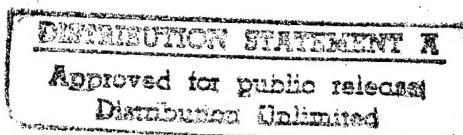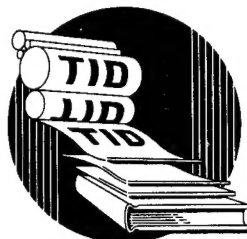
By
L. Eyring
B. B. Cunningham
H. R. Lohr

July 7, 1950

University of California Radiation Laboratory

Technical Information Division, ORE, Oak Ridge, Tennessee

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HEATS OF REACTION OF SOME OXIDES OF AMERICIUM AND PRASEODYMIUM WITH NITRIC ACID AND AN ESTIMATE OF THE POTENTIALS OF THE Am(III)-Am(IV) AND Pr(III)-Pr(IV) COUPLES

L. Eyring,[*] B. B. Cunningham, and H. R. Lohr[**]
Department of Chemistry and Radiation Laboratory
University of California, Berkeley, California

July 7, 1950

It has been shown previously[1] that the potential of the Am(III)-Am(IV) couple in acid solution is more negative than -2.0v. The work described in this paper was undertaken for the purpose of evaluating the magnitude of the potential more precisely. It seems scarcely necessary to remark that an extensive correlation of the chemical properties of an element is possible when its oxidation potentials are known. The chemistry of americium possesses special interest in that it is the first of the transuranium elements in which the stability of the tripositive state is comparable to that observed for some of the lanthanide elements.

In the course of development of this work it was necessary that a less costly and less hazardous material be employed as a "stand-in" in perfecting the techniques

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[*]Now at the Department of Chemistry, State University of Iowa, Iowa City, Iowa. Part of the data reported here was included in a dissertation submitted by L. Eyring to the Graduate Division of the University of California in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[**]Present address: Argonne National Laboratories, Chicago, Illinois.

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(1) Cunningham, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 19.2 (McGraw-Hill Book Co., Inc., New York, 1949).

which were intended ultimately to be applied to americium. Praseodymium was chosen
for this purpose, primarily because existing information indicated that the
Pr(III)-Pr(IV) potential probably would not differ greatly from that of the
corresponding americium couple. The work reported here permits a reasonably
accurate evaluation of the potential of the (III)-(IV) couple of praseodymium
as well as that of americium.

Since it was known that the potential of the americium couple was so negative
as to make the tetrapositive state highly unstable in aqueous solution, it did
not appear feasible to measure the potential in the conventional manner by in-
corporating the couple in a reversible chemical cell.

We chose, therefore, to evaluate the free energy of this reaction by the
less direct and somewhat less accurate method of evaluating its heat and estimating
the entropy change.

Unless otherwise noted, our ΔH and ΔS values refer to a temperature of $298^\circ K$.
Results are expressed in kcal./mole for the reaction as written, and values of
ΔH and ΔS are given only to the nearest 0.1 kcal. or 0.1 e.u., consistent with
the accuracy of the experimental measurements.

Accepted values for heats of formation, etc., are in most cases those given
in "Selected Values of Chemical Thermodynamic Properties," (abbreviated SVCTP)
issued by the National Bureau of Standards.

Our results are not corrected to unit activities, since the activity co-
efficients of the +3 ions in our solutions are not known. Consequently, our
derived values are not designated as $\Delta H_f^{\,o}$ values.

Such corrections probably are negligible compared with our experimental
errors of several tenths of a kilocalorie.

EXPERIMENTAL

Preparation of $Pr_2O_3{}_{(c)}$ and Measurements of Its Heat of Reaction

With 6$\underline{M}$ Nitric Acid

Bichowski and Rossini[2] record data obtained by Prandtl and Huttner[3] in 1925 on the heats of reaction of $Pr_2O_3{}_{(c)}$, $Pr_6O_{11}{}_{(c)}$, and $PrO_2{}_{(c)}$ with $HNO_3(6)$. Because of the difficulty of obtaining pure samples of the rare earths prior to the development of modern ion exchange methods[4] there is reason to question much of the early work on the chemistry of these elements. Our measurements on praseodymium were therefore made as accurately as possible with the equipment available to us.

The praseodymium used in the experiments described herein was obtained as "spectrographically pure Pr_2O_3" from Johnson, Matthey and Co., Ltd., of London. This material was found to contain about four percent of sodium and potassium, and one-half of one percent of other rare earths, principally neodymium. This relatively pure oxide was further purified by D. C. Stewart and R. C. Lilly of this Laboratory by a cation-exchange column separation procedure using Dowex-50 resin. No impurities were detected by spectrographic analysis of a 50 μg sample. Elements analyzed for, and their limits of detection in micrograms, were as follows: Al, 0.01; Ba, 0.1; Be, 0.005; Ca, 0.01; Ce, 0.1; Dy, 0.1; Er, 0.1; Eu, 0.01; Fe, 0.05; Gd, 0.1; Ho, 0.1; K, 0.1; La, 0.01; Lu, 0.01; Na, 0.1; Nd, 0.05; Sm, 0.1; Sr, 0.01; Ta, 0.5; Tb, 0.1; Yb, 0.01; Y, 0.01.

(2) Bichowski and Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corporation, New York (1936).

(3) Prandtl and Huttner, Z. anorg. allgem. Chem. 149, 235 (1925).

(4) Harris and Tompkins, J. Am. Chem. Soc. 69, 2792 (1947); Ketelle and Boyd, ibid., 2800; Spedding, Voigt, Gladrow, Sleight, Powell, Wright, Butler, and Figard, ibid., 2786.

The praseodymium from the column runs was precipitated as oxalate from

$0.1\underline{M}$ HCl-$0.25\underline{M}$ NH_4Cl-$0.25\underline{M}$ H_3Cit solution by the addition of oxalic acid to

$0.1\underline{M}$. The praseodymium oxalate was ignited in air to the black oxide usually

called "Pr_6O_{11}." The ignition was carried out in a platinum container at about

650°C. This oxide constituted the stock material from which the succeeding

praseodymium calorimeter samples were prepared.

The oxide was placed in the hydrogen reduction apparatus shown in Fig. 1

and pumped down to remove all adsorbed moisture. The molybdenum radiation shield

used to heat the oxide sample in the reduction apparatus was found to resist

the action of hydrogen at these high temperatures to a much greater degree than

tungsten, tantalum, cold rolled steel or stainless steel. The chromel vs. alumel

thermocouple was spot welded to the bottom of the platinum sample holder. About

one-third atmosphere of pure hydrogen was admitted from a tube of uranium hydride

maintained at 360°C.

The oxide charge was heated to 500°C. and maintained at that temperature

throughout the reduction. After two or three minutes the black oxide began to

change to yellow-green Pr_2O_3. From time to time the sample container was removed

from the reduction apparatus, capped and weighed on an Ainsworth FDJ microbalance.

No further decrease in weight was observed after one hour of heating with hydrogen.

Therefore, an adequate time of one and one-half hours was adopted for the reduction

to Pr_2O_3. X-ray diffraction results on this material consistently showed it to

be the cubic C form with a = 11.14 ± 0.01 Å. When the temperature of this product

was increased to 1000°C. in vacuum it changed over to the pale green hexagonal A

form with a = 3.859 ± 0.003 Å, c = 6.008 ± 0.003 Å. If the Pr_6O_{11} was reduced at

1000°C., the A form was produced directly. The reaction at lower temperature may

be represented as:

$$Pr_6O_{11(c)} + 2H_{2(g)} \xrightarrow[500^oC.]{1/3 \text{ atm. } H_2} 3Pr_2O_{3(c)} + 2H_2O_{(g)} \qquad (1)$$

C Form
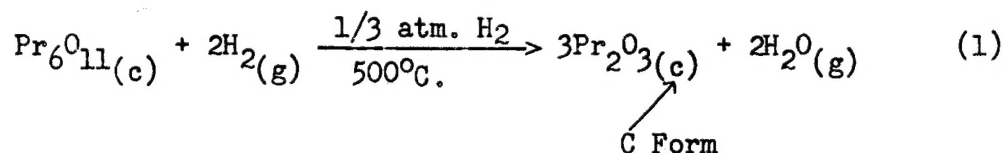
Praseodymium sesquioxide prepared as described above was removed immediately into the dry atmosphere of a nitrogen "dry box." There it was quickly loaded into weighed sample bulbs and sealed off with Apiezon "W" wax ready for reweighing and calorimetric runs. The weighings were carried out on a quartz fiber torsion balance similar to that described by Kirk, Craig, Gullberg, and Boyer.[5] The instrument had a sensibility of $\pm$ 0.01 μg and an accuracy of calibration of $\pm$ 0.1%.

The microcalorimeter used for the heat measurements was that described by Westrum.[6] It was not suited to the measurement of heats developed over a time longer than a very few minutes. It was essential, therefore, that the oxides be prepared in readily soluble form.* Preliminary experiments mentioned below showed that AmO_2 could not be prepared in any form which would dissolve rapidly in nitric acid more dilute than 6M. Praseodymium sesquioxide prepared as described above was found to dissolve in 6.02M nitric acid in about two minutes. The first heat measurements were made, therefore, in 6.02M nitric acid.

The results of the determination of the heat of solution of praseodymium sesquioxide in 6.02M HNO_3 at 25^oC. are given in Table I.

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*In general, oxides prepared at low temperatures dissolve much more rapidly than those prepared at higher temperatures, probably because of smaller particle size. It is recognized that the heat content of such finely divided material may be appreciably different (perhaps of the order of a kilocalorie) from that of oxide prepared at higher temperatures (Giauque, J.Am.Chem. Soc., 71, 3192 (1949).

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(5) Kirk, Craig, Gullberg, and Boyer, Anal. Chem. 19, 427 (1947).

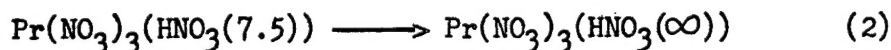(6) Westrum, U. S. Atomic Energy Commission Declassified Document AECD-1903 (1948).

Table I

Heat of Reaction of Pr_2O_3 (C form) with 6.02$\underline{M}$ HNO_3 at 25°C.

Run No.	Weight Mg	Heat Evolved Calories	ΔH kcal./mole
1	7.312	2.355	-106.2
2	4.109	1.324	-106.3
3	4.539	1.459	$\underline{-106.0}$
			-106.2 ± 0.2

In order to estimate the heat for the reaction:

$$Pr(NO_3)_3(HNO_3(7.5)) \longrightarrow Pr(NO_3)_3(HNO_3(\infty)) \qquad (2)$$

additional measurements were made of the heat of reaction of $Pr_2O_{3(c)}$ with 1.0$\underline{M}$ nitric acid. These measurements are summarized in Table II below:
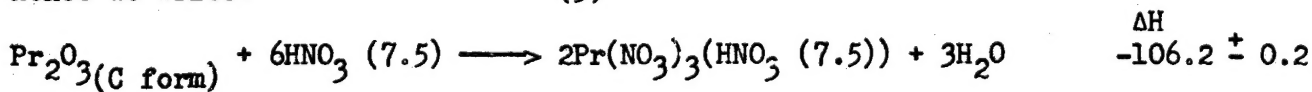
Table II

Heat of Reaction of $Pr_2O_{3(C\ form)}$ with 1.0$\underline{M}$ HNO_3 at 25°C.

Run No.	Weight Mg	Heat Evolved Calories	ΔH kcal./mole
1	3.825	1.136	-97.9
2	10.769	3.180	-97.4
3	3.081	0.897	$\underline{-96.0}$
			-97.1 ± 0.7

Hence we write: $\qquad\qquad (3)$

$$Pr_2O_{3(C\ form)} + 6HNO_3\ (7.5) \longrightarrow 2Pr(NO_3)_3(HNO_3\ (7.5)) + 3H_2O \qquad \begin{array}{c}\Delta H \\ -106.2 \pm 0.2\end{array}$$

and $\qquad\qquad (4)$

$$Pr_2O_{3(C\ form)} + 6HNO_3\ (54) \longrightarrow 2Pr(NO_3)_3(HNO_3\ (54)) + 3H_2O \qquad -97.1 \pm 0.7$$
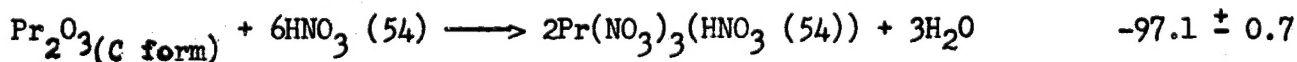
We neglect the heats for the following reactions:

$$3H_2O \ (HNO_3 \ (7.5)) \longrightarrow 3H_2O \ (HNO_3 \ (\infty)) \tag{5}$$

$$3H_2O \ (HNO_3 \ (54)) \longrightarrow 3H_2O \ (HNO_3 \ (\infty)) \tag{6}$$

$$Pr(NO_3)_3 \ (\sim 10,000 \ HNO_3 \ (7.5)) \longrightarrow Pr(NO_3)_3 \ (\infty \ HNO_3 \ (7.5)) \tag{7}$$

$$Pr(NO_3)_3 \ (\sim 10,000 \ HNO_3 \ (54)) \longrightarrow Pr(NO_3)_3 \ (\infty \ HNO_3 \ (54)) \tag{8}$$
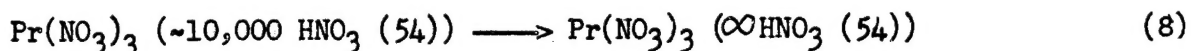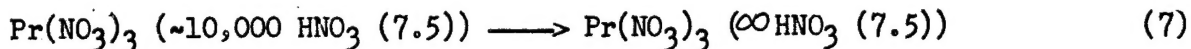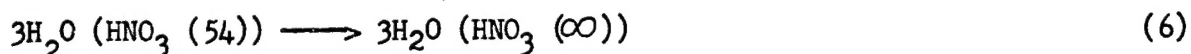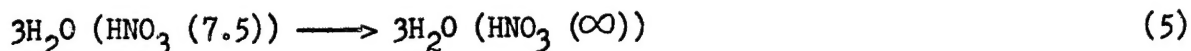
From equation (3) we calculate the heat of formation of $Pr(NO_3)(HNO_3 \ (7.5))$ as:

$1/2 \ (-106.2 + 3 \times 68.3 - 6 \times 48.8 - 444.5) = -319.3$ kcal./mole

and from equation (4) the heat of formation of $Pr(NO_3)_3(HNO_3 \ (54))$ as:

$1/2 \ (-97.1 + 3 \times 68.3 - 6 \times 49.2 - 444.5) = -316.0$ kcal./mole,

based on values for the heats of formation of $H_2O_{(1)}$, $Pr_2O_{3(c)}$, $HNO_3 \ (7.5)$

and $HNO_3 \ (54)$ taken from SVCTP. We estimate the heat of formation of $Pr(NO_3)_{3(aq)}$

to be -315.5 kcal./mole at $298^\circ K$, and the heat of formation of $Pr^{+3}_{(aq)}$ to

be $-315.5 + 3 \times 49.4 = -167.3$ kcal./mole.

Preparation of PrO_2 and Measurement of Its Heat of Reaction with 6M Nitric Acid

Praseodymium dioxide was prepared from the sesquioxide by heating the latter in a quartz bomb in a high pressure of oxygen gas.

The bomb consisted of a thick walled quartz tube of about 8 mm. OD and 2-3 mm. ID with a rounded bottom and a constricted portion at the other end. The constriction insured a thick wall when the end was sealed.

The Pr_2O_3 was loaded into the bomb and the open end attached to a system which was alternately evacuated and flushed with oxygen from which water and carbon dioxide were removed previously by passing the gas through a copper coil kept at $-100^\circ C$. by an alcohol-liquid nitrogen mixture. Finally, with oxygen in the bomb, the end was immersed in liquid nitrogen and oxygen was liquified in

an amount previously calculated to produce 100 atmospheres pressure in the tube at 500°C. At this point the bomb was sealed off with a gas-oxygen flame. The quartz bomb was then placed in a stainless steel jacket which served as protection against a possible explosion. The complete assembly was put into a muffle furnace and heated at 500°C. for 8-12 hours. The resulting product was a reddish-black mono-phasic substance having a fluorite type structure, with a = 5.395 $\pm$ 0.005 $\overset{\circ}{A}$.

The oxide was transferred to a small phosphorus pentoxide desiccator inside a "dry box" ready for loading into calorimeter bulbs.

The results of calorimetric measurements on this material are given in Table III.

Table III
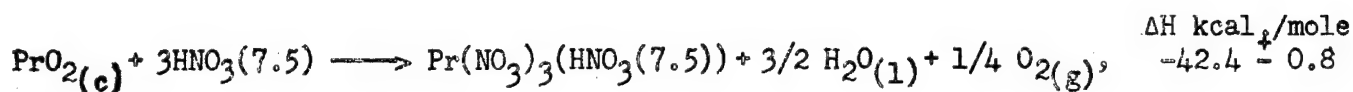### Heat of Reaction of PrO_2 with 6.02$\underline{M}$ HNO_3 at 25°C.

Run No.	Weight Mg	Heat Evolved Calories	ΔH kcal/mole
1	1.0042	0.2381	-41.0
2	0.5712	0.1412	-42.8
3	0.4722	0.1186	-43.4
4	0.8412	0.2071	-42.6
			-42.4 $\pm$ 0.8

The solution time for these samples was from fifteen to twenty minutes and the drift correction amounted to some ten to twenty-five percent of the observed heat. This fact leads to a greater uncertainty than that indicated by the mean deviation given above.

From the above data we calculate the heat of formation of $PrO_{2(c)}$[*] on the basis of the following reaction:[**]   (9)

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[*]X-ray diffraction measurements showed the lattice constant of the oxide produced by heating with high pressures of oxygen to be 5.394 $\pm$ 0.002 $\overset{\circ}{A}$ as compared with 5.468 $\pm$ 0.001 $\overset{\circ}{A}$ for "Pr_6O_{11}." The decrease in lattice constant is that expected for complete oxidation to PrO_2, within the experimental error of the measurements.

[**]It has been shown by Prandtl and Huttner[1] that the only products of the reaction between $PrO_{2(c)}$ and $HNO_{3(6)}$ are $Pr(NO_3)_3$, H_2O and O_2.

$$PrO_{2(c)} + 3HNO_3(7.5) \longrightarrow Pr(NO_3)_3(HNO_3(7.5)) + 3/2\ H_2O_{(1)} + 1/4\ O_{2(g)},$$

$$\begin{matrix} \Delta H\ kcal./mole \\ -42.4 \pm 0.8 \end{matrix}$$
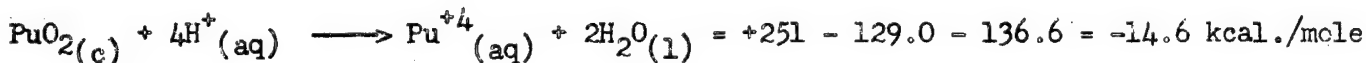
$$\Delta Hf = -319.3 - 102.4 + 146.4 + 42.4 = -232.9\ kcal./mole$$

We estimate ΔH_{298} for the reaction:

$$PrO_{2(c)} + 4H^+ (\infty) \longrightarrow Pr^{+4}_{(aq)} + 2H_2O_{(1)} \qquad (10)$$
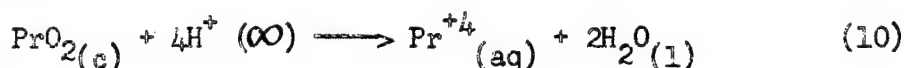
by analogy with the corresponding plutonium reaction, as follows.
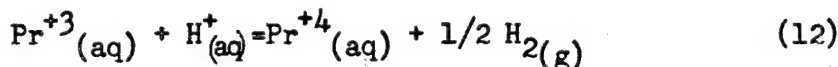
Brewer, Bromley, Gilles, and Lofgren[7] give for the heat of formation of $Pu^{+4}_{(aq)}$ and $PuO_{2(c)}$ at $298°K$, -129.0 and -251 kcal./mole, respectively, whence ΔH_{298} for the reaction: (11)

$$PuO_{2(c)} + 4H^+_{(aq)} \longrightarrow Pu^{+4}_{(aq)} + 2H_2O_{(1)} = +251 - 129.0 - 136.6 = -14.6\ kcal./mole$$

Since PuO_2 and PrO_2 have identical crystal structures and very nearly the same lattice dimensions, we believe that the difference between the lattice energy of PuO_2 and the energy of hydration of Pu^{+4} on the one hand and of PrO_2 and Pr^{+4} on the other will be nearly the same and that, therefore, the heat of reaction (10) will not differ from that of reaction (11) by more than a kilocalorie.

We therefore take the heat of reaction (10) to be -14.6 kcal./mole whence, from our calculated value of the heat of formation of $PrO_{2(c)}$, we calculate the heat of formation of $Pr^{+4}_{(aq)}$ to be $-232.9 - 14.6 + 136.6 = -110.9$ kcal./mole. For the reaction:

$$Pr^{+3}_{(aq)} + H^+_{(aq)} = Pr^{+4}_{(aq)} + 1/2\ H_{2(g)} \qquad (12)$$

$$\Delta H_{298} = -110.9 + 167.3 = +56.4\ kcal.$$

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(7) Brewer, Bromley, Gilles, and Lofgren, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 6.40 (McGraw-Hill Book Co., Inc., New York, 1949).

Estimation of ΔS for the Reaction $Pr^{+3}_{(aq)} + H^{+}_{(aq)} = Pr^{+4}_{(aq)} + 1/2\ H_{2(g)}$

Our estimate of ΔS for reaction (12) is <u>based on analogy with the correspond-</u><u>ing plutonium reaction</u>, which has been investigated by Evans.[8] Evans reports

$$S_{Pu}{+4} - S_{Pu}{+3} = -48.0 \text{ cal./degree}$$

The work of Howland and Calvin[9] on the magnetic susceptibilities of the

plutonium ions indicates that about 0.3 e.u. of the ΔS value given above is due to

a magnetic contribution. Correcting $S_{Pr}{+4} - S_{Pr}{+3}$ for the magnetic contributions,

we estimate:

$$S_{Pr}{+4} - S_{Pr}{+3} = -48.3 - 0.8 = -49.1 \text{ cal./degree.}$$

Although the absolute entropies of Pr^{+3} and Pu^{+3}, of Pr^{+4} and Pu^{+4} will be some-

what different, we believe that ΔS for the two reactions will differ significantly

only in the magnetic terms since the ionic radii of the corresponding ions are

nearly the same, and the mass correction cancels. Hence we now write:

$Pr^{+3}_{(aq)} + H^{+}_{(aq)} = Pr^{+4}_{(aq)} + 1/2\ H_{2(g)}$	ΔH_{298} kcals.	ΔS_{298} e.u.	ΔF_{298} kcals.
	+56.4	−49.1	+66.4
		+15.6	
		−33.5	

and $E = -\dfrac{\Delta F}{nF} = \dfrac{-66.4}{23.07} = -2.88v$

In the above calculations we have made no attempt to correct for activity co-

efficients since there are no satisfactory experimental data on which to base

such a correction.

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(8) Evans, <u>ibid</u>., Paper No. 3.30.

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                  and
(9) Howland Calvin, J. Phys. Chem., in press.

Preparation of AmO$_2$ and Measurement of its Heat of Reaction

The americium used in these experiments was obtained from β^--decay of Pu^{241} produced by successive (n,γ) reactions on Pu^{239} irradiated with pile neutrons.[10]

The separation, concentration, and purification of americium from a source of this kind has been described elsewhere.[1] The results of a spectrographic analysis of our americium stock solution are given in Table IV.

Table IV

Spectrographic Analysis
Microgram per 50 microgram sample

Al <0.01	Fe <0.1
Be <0.005	K <0.1
Ca 0.02	Mn <0.01
Ce <0.1	Na <0.01
Cr <0.01	Ni < 0.01
	Pb <0.1

The americium was precipitated with a small excess of pure oxalic acid and the dried oxalate decomposed in air at a temperature of 650°C. This treatment produced a black dioxide which was very slowly soluble under all conditions tried. The black AmO$_2$ was reduced with hydrogen at 600°C. in the apparatus previously described, forming Am$_2$O$_3$ (identified by x-ray diffraction analysis). The sesquioxide is a bright persimmon (bright red-orange) colored compound.

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(10) Seaborg, Phys. Rev. 78, 472 (1950).

No evidence for the formation of AmO, reported by Fried,[11] was obtained in these experiments.

The sesquioxide was heated in air at about 250°C. for one hour producing AmO_2 in a form soluble in $6\underline{M}$ HNO_3 $0.1\underline{M}$ HBF_4 (but not in $6\underline{M}$ HNO_3 alone) in a sufficiently short time to be satisfactory for calorimetric measurements. The dioxide possessed the same fluorite type structure as PrO_2 with a = 5.393 ± 0.005 $\overset{o}{A}$. It has been shown by Asprey and Cunningham[12] that the composition of the oxide obtained under these conditions is $AmO_{1.98 \pm 0.02}$.

Four runs were made in the calorimeter on AmO_2 yielding the values of ΔH indicated in Table V.

Table V

Heat of Reaction of AmO_2 with $6.0\underline{M}$ HNO_3, $0.1\underline{M}$ HBF_4
at 25°C.

Run No.	Weight Mg	Heat Evolved Calories	ΔH kcal./mole
1	0.834	0.09062	-29.7
2	0.672	0.07466	-30.3
3	1.177	0.1326	-30.8
4	1.449	0.1636	-30.8
			-30.4 $\pm$ 0.4

In order to investigate the possible heat effect of the fluoboric acid on the reaction we measured the heat of reaction of PrO_2 with HNO_3 (7.5), HBF_4 (550).

(11) Fried, private communication (1948).

(12) Asprey and Cunningham, to be published.

The results are summarized in Table VI below.

Table VI

Heat of Reaction of PrO$_2$ with 6.0$\underline{M}$ Nitric Acid, 0.1$\underline{M}$ Fluoboric Acid at 25°C.

Run No.	Weight Mg	Heat Evolved Calories	ΔH kcal./mole
1	0.827	0.2002	-41.9
2	1.430	0.3471	-42.0
3	1.229	0.3031	-42.7
4	1.177	0.2818	<u>-41.4</u>
			42.0 ± 0.4

Within experimental error the mean value of the heat is the same as that found in HNO$_3$ (7.5) alone. We therefore assume that the heat of reaction of AmO$_2$ or PrO$_2$ with HNO$_3$ (7.5), HBF$_4$ (550) is not significantly different from that with HNO$_3$ (7.5) alone.

We take the heat for the reaction:

$$\text{AmO}_{2(c)} + 4\text{H}^+_{(aq)} \longrightarrow \text{Am}^{+4}_{(aq)} + 2\text{H}_2\text{O}_{(1)} \qquad (13)$$
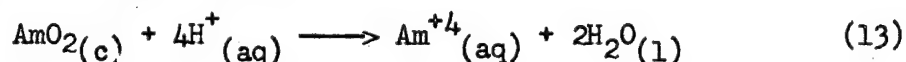
to be -14.6 kcal./mole, the same as that for the corresponding plutonium reaction, and the heat for the reaction

$$\text{Am(NO}_3)_3(\text{HNO}_3(7.5)) \longrightarrow \text{Am(NO}_3)_3(\text{HNO}_3 \ (54)) \qquad (14)$$
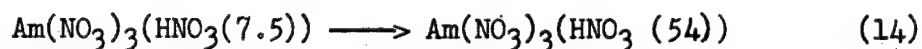
to be the same as that for the corresponding praseodymium reaction, namely +3.3 kcal./mole.

As in the case of praseodymium we neglect the heats corresponding to those reactions listed as (5), (6), (7), and (8) appearing in the section describing the measurement of the heat of reaction of Pr$_2$O$_{3(c)}$ with six molar nitric acid.

Our estimate of the heat of the reaction: $Am^{+3}_{(aq)} + H^+_{(aq)} = Am^{+4}_{(aq)} + 1/2\ H_{2(g)}$ (15)

will therefore differ from that estimated for the corresponding praseodymium

reaction only by the difference in the heats of reaction of PrO_2 and AmO_2 with

six molar nitric acid. This difference amounts to $+30.4 - 42.4 = 12.0$ kcals.

We therefore estimate ΔH_{298} for reaction (15) to be:

$$+56.4 - 12.0 = 44.4 \text{ kcal./mole}$$

Our estimate of ΔS_{298} for reaction (15) again is based on that for the correspond-

ing plutonium reaction, after making a correction for magnetic entropy based on

the work of Howland and Calvin.

Whence we estimate ΔS_{298} for reaction (15) to be:

$$-48.3 + 1.4 + 15.6 = -31.3 \text{ e.u.}$$

ΔF_{298} for reaction (15) is therefore :

$$44.4 + \frac{298}{1000}\ 31.3 = 53.7 \text{ kcal./mole,}$$

$$\text{and } E = \frac{-53.7}{23.1} = -2.32v.$$

DISCUSSION

Our calculations of the heats of formation of $Pr(NO_3)_3(HNO_3\ (7.5))$,

$Pr(NO_3)_3(HNO_3\ (54))$ and of $Pr^{+4}_{(aq)}$ are all based on an accepted value of -444.5

kcal. for the heat of formation of $Pr_2O_{3(c)}$. Any revision of this value will require

a corresponding revision of our calculated values. Our justification for several

estimations of ΔH and ΔS values by analogy between praseodymium, plutonium and

americium is based on the fact that the ionic radii, structures and types of

bonding in analogous compounds and ions of these elements are known to be closely

similar.

*   It is evident that the potentials of the $Pr^{+3}-Pr^{+4}$ and $Am^{+3}-Am^{+4}$ couples

are so negative as to make it difficult, if not impossible, to obtain observable

concentrations of these ions in aqueous solution. This conclusion is consistent with the failure of numerous attempts[1] to obtain substantial concentrations of the +4 ion by oxidation in aqueous solution. Presumably such attempts could succeed only in the presence of complexing or precipitating agents capable of forming very stable complexes or very insoluble compounds of the tetrapositive ion.

There is some evidence that oxidation of americium from the plus three to the plus four state can occur in the presence of peroxide in alkaline solution. This is not inconsistent with the potential of the peroxide-water couple and the estimated solubility products of $Am(OH)_3$ and $Am(OH)_4$, which would not be expected to be very greatly different than those listed by Latimer[13] for $La(OH)_3$ and $Th(OH)_4$.

It is of some interest to compare the oxidation potential of the Am^{+3}-Am^{+4} couple with that of preceding elements of the actinide series. The data are summarized in Table VII.

Table VII

Oxidation Potentials of the III-IV Couples of Various Actinide Elements[14]

Couple	Potential (volts)
U(III)-U(IV)	+0.64
Np(III)-Np(IV)	-0.14
Pu(III)-Pu(IV)	-0.97
Am(III)-Am(IV)	-2.3

(13) Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N.Y., 1938.

(14) Seaborg, Nucleonics 5, No. 5, 17 (1949).

The potential of the Np(III)-Np(IV) couple is almost exactly midway between that of the U(III)-U(IV) and Pu(III)-Pu(IV) couples. It has been suggested by Brewer[15] that this is due to a regular increase in the ionization potential of the fourth electron in succeeding members of the actinide series. The pronounced deviation of americium from this regularity indicates that this suggestion may not be correct. However, the magnitude of the potential in each case depends upon a relatively small difference between large energy terms (the heats of sublimation and hydration of the ions and the ionization potentials) and small irregularities in the trends in any of these terms would suffice to obscure regularities in the other terms.

The value of the potential of the Am^{+3}-Am^{+4} couple may be used to estimate the free energies of other reactions involving the tri and tetrapositive states.

For example, if we assume that the difference between the free energies of $Pu^{+3}_{(aq)}$ and $Pu^{+4}_{(aq)}$ on the one hand and of $Am^{+3}_{(aq)}$ and $Am^{+4}_{(aq)}$ also extend to their fluorides we calculate from the data of Brewer, Bromley, Gilles and Lofgren[7] on the free energies of formation of PuF_3 and PuF_4 that ΔF_{298} for the reaction:

$$AmF_4 \longrightarrow AmF_3 + 1/2\ F_2 \qquad\qquad (16)$$
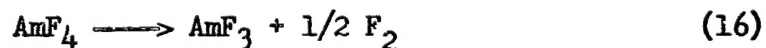
is equal to +11.8 kcals. Taking the entropy for the reaction to be the same as that for the corresponding plutonium reaction, 16 e.u., we estimate ΔF_{1000} to be +0.6 kcal. It should be possible to prepare stable AmF_4 by treatment of the trifluoride with fluorine and also to investigate the equilibrium experimentally.


(15) Brewer, U. S. Atomic Energy Commission Declassified Document AECD-1899 (1948).

No other solid halides of tetrapositive americium will be stable.

Finally it is emphasized that our considerations apply only to the tetra-positive state of americium. Solid compounds of Am(V) and Am(VI) are known.[16,17]

The stability of the ions of these higher oxidation states is undoubtedly due to the large negative free energy values for the reactions:

$$Am^{+5} + 2H_2O \longrightarrow AmO_2^{+} + 4H^{+} \tag{17}$$

and

$$Am^{+6} + 2H_2O \longrightarrow AmO_2^{++} + 4H^{+} \tag{18}$$
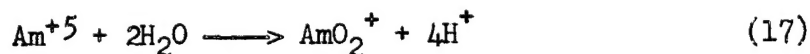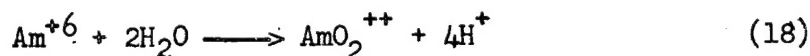
SUMMARY

The heats of reaction at $25^{\circ}C$. of $Pr_2O_{3(C\ form)}$ with $6.02\underline{M}$ nitric acid and with $1.0\underline{M}$ nitric acid were found to be -106.2 ± 0.2 and -97.1 ± 0.7 kcal./mole, respectively. From these measurements and an accepted value of -444.5 kcal. for the heat of formation of $Pr_2O_{3(c)}$ the heats of formation of $Pr(NO_3)_3(HNO_3(7.5))$ and $Pr(NO_3)_3(HNO_3 (54))$ are calculated to be -319.3 ± 0.3 and -316.0 ± 0.8 kcal., respectively. A value of -315.5 ± 1 kcal. is estimated for the heat of formation of $Pr(NO_3)_3(HNO_3 (\infty))$ and from this -167.3 ± 1 kcal. for the heat of formation of $Pr^{+3}_{(aq)}$.

The heats of reaction of $PrO_{2(c)}$ with $6.02\underline{M}$ nitric acid and with $6.0\underline{M}$ nitric acid - $0.1\underline{M}$ fluoboric acid were measured as -42.4 ± 0.8 and -42.0 ± 0.4 kcal., respectively. The heat of formation of $PrO_{2(c)}$ is calculated to be -232.9 ± 1.0 kcal.

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(16) Werner and Perlman, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 22.5 (McGraw-Hill Book Co., Inc., New York, 1949).

(17) Asprey, Stephanou, and Penneman, J. Am. Chem. Soc. 72, 1425 (1950).

The heat of the reaction: $PrO_{2(c)} + 4H^+(aq) \longrightarrow Pr^{+4}(aq) + 2H_2O_{(1)}$ is estimated to be -14.6 ± 1 kcal., by analogy with the corresponding plutonium reaction, and the heat of formation of $Pr^{+4}(aq)$ to be -110.9 ± 1.5 kcal.

The heat of the reaction: $Pr^{+3}(aq) + H^+(aq) \longrightarrow Pr^{+4}(aq) + 1/2\ H_{2(g)}$ is estimated to be $+56.4 \pm 1.7$ kcal. and the entropy -33.5 ± 1 e.u. Hence ΔF_{298} is equal to $+66.4 \pm 2$ kilocalories and $E = -2.88 \pm 0.1$v.

The heat of reaction of AmO_2 with $6.0\underline{M}$ nitric acid - $0.1\underline{M}$ fluoboric acid was measured as -30.4 ± 0.4 kcals.

The heat of the reaction: $Am^{+3}(aq) + H^+(aq) \longrightarrow Am^{+4}(aq) + 1/2\ H_{2(g)}$ is estimated to be $+44.4 \pm 2$ kcals. and ΔS as -31.3 cal./degree. Hence, for this reaction, $\Delta F_{298} = +53.7 \pm 2$ kcals. and $E = -2.32 \pm 0.1$v.

ΔF_{298} for the reaction: $AmF_4 \longrightarrow AmF_3 + 1/2\ F_2$ is estimated to be $+11.8$ kcals. and ΔF_{1000} to be $+0.6$ kcal.

ACKNOWLEDGMENT

TOP VIEW
Mo SHIELD
W SUPPORTS
Pt PLATFORM
SAMPLE CONTAINER

OPTICAL PORT
INDUCTION COIL
Mo SHIELD
PLATFORM
SAMPLE CONTAINER
THERMOCOUPLE

HANGER
TO HYDROGEN OR ARGON
SOFT Fe IN GLASS

$^{50}/_{50}$ STD TAPER

GROUND GLASS DISK

TOP EDGE GROUND

$^{34}/_{45}$ STD TAPER

TO VACUUM

THERMOCOUPLE
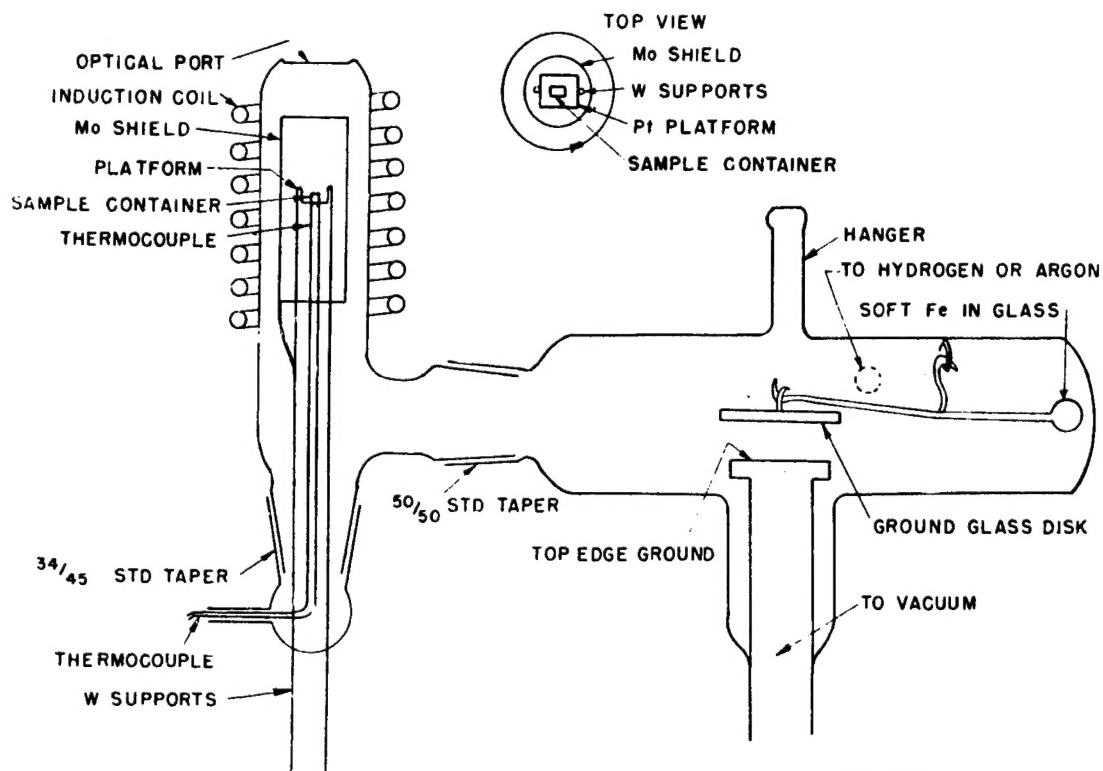W SUPPORTS

FIG. I   MU 518

HYDROGEN REDUCTION APPARATUS

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